

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08G 59/42, C09D 163/00, C08L 73/02		A1	(11) International Publication Number: WO 96/01864 (43) International Publication Date: 25 January 1996 (25.01.96)
(21) International Application Number: PCT/US95/07123 (22) International Filing Date: 16 June 1995 (16.06.95) (30) Priority Data: 08/272,343 8 July 1994 (08.07.94) US (60) Parent Application or Grant (63) Related by Continuation US 08/272,343 (CON) Filed on 8 July 1994 (08.07.94) (71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): BARSOTTI, Robert, J. [US/US]; R.D. 2, Box 163A, Coles Mill Road, Franklinville, NJ 08322-9517 (US). HARPER, Lee, R. [US/US]; 330 South Old Middletown Road, Media, PA 19063-4751 (US). (74) Agents: COSTELLO, James, A. et al.; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).			(81) Designated States: BR, CA, CN, JP, KR, MX, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: LOW VOC REFINISH COATING COMPOSITION (57) Abstract A coating composition based on low molecular weight anhydride resin having pendant, non-cyclic anhydride moieties, hydroxy-functional epoxy resin, and active catalyst exhibits excellent performance characteristics as a coating cured at ambient conditions.			

BEST AVAILABLE COPY

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

TITLE**LOW VOC REFINISH COATING COMPOSITION**

5

BACKGROUND OF THE INVENTION

The present invention relates to a curable coating composition particularly useful as a top coat in multi-layered coating systems.

Base coat-clear coat systems have found wide acceptance in the past decade as automotive finishes. Continuing effort has been directed to such coatings systems to improve the overall appearance, the clarity of the top coat, and the resistance to deterioration. Further effort has been directed to the development of coating compositions having low volatile organic content (VOC) and which cure at ambient temperature.

Previous efforts at improving the etch resistance and durability of coatings had suggested the use of anhydride resins having pendant non-cyclic anhydride moieties in combination with resins that react with the polyanhydride resins to cure under curing conditions. However, a continuing need exists for coating formulations which can be sprayed at low VOC and which exhibit outstanding performance characteristics after application, and particularly resistance to environmental etching, and which

20

cure at room temperature or ambient conditions.

SUMMARY OF THE INVENTION

The present invention provides a sprayable coating composition which can be easily applied at high solids and exhibits outstanding appearance and durability after application and ease of maintenance.

Specifically, the instant invention provides a curable coating composition for curing at ambient conditions comprising organic solvent and binder comprising

30

(a) an anhydride resin having a molecular weight of less than about 3000 that contains (1) a central moiety, and (2) on average, more than one pendant, non-cyclic anhydride moiety bonded to each central moiety;

(b) An oligomer or polymer having a molecular weight of 150 to 20,000 and having epoxy functionality of at least 2, at least a portion of

35

which oligomer or polymer has at least one hydroxy functionality to enable curing at ambient conditions;

(c) an optional amount of an isocyanate crosslinking agent; and

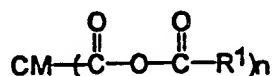
(d) A functional effective amount of at least one active catalyst,

5 and

wherein the ratio of equivalents of hydroxy to anhydride is at least 0.05 to 1.0.

DETAILED DESCRIPTION OF THE INVENTION

10 The compositions according to the present invention comprise anhydride resins having a (weight average) molecular weight of less than about 3000 and having a central moiety with more than one pendant, non-cyclic anhydride moiety bonded to each central moiety. This anhydride can suitably be used in the amount of 10 to 80 percent by weight of binder,
15 preferably 35 to 60 percent. The anhydride is asymmetrical, and preferably contains a moiety represented by the following formula:



20 wherein (CM) is a central moiety, (R¹) is an organic moiety, and n is a number of pendant anhydride groups that averages greater than one.

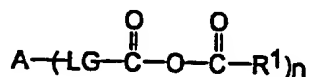
The central moiety can be a simple organic moiety, such as an aliphatic, cycloaliphatic or aromatic moiety, with a plurality of anhydride groups bonded to it. Alternatively, it can contain a plurality of repeating
25 units which are bonded to one or more pendant anhydride groups. Examples of suitable non-polymeric central moieties are those derived from multifunctional alcohols such as pentaerythritol, trimethylolpropane and neopentyl glycol. The multifunctional alcohols are reacted with cyclic, monomeric anhydride such as methyl hexahydrophthalic anhydride to give a
30 multifunctional acid containing moiety. The resulting product is then reacted with ketene to form the linear pendant anhydride.

The central moiety is linked to more than one non-cyclic anhydride moiety, on average. It is preferably linked to at least about 2

non-cyclic anhydride groups on average and more preferably to at least about 3 non-cyclic anhydride groups on average. The anhydride equivalent weight (formula weight per anhydride group) is preferably at least about 200 and preferably no more than about 1000.

5 Each anhydride moiety is typically terminated by an organic group (R^1). This group is preferably aliphatic and more preferably alkyl. It preferably contains no more than about 6 carbon atoms, more preferably no more than about 4 carbon atoms, and most preferably methyl.

10 The oligomeric anhydride can optionally contain a polyvalent organic moiety (A) that is linked to a plurality of anhydride groups by a plurality of pendant linking groups (LG), as illustrated in the following formula:

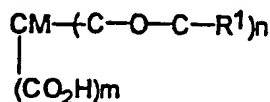


15

The linking group (LG) can contain, for example, ester linkages, alkylene groups, ether linkages, urethane linkages and combinations of those. The polyvalent organic group can contain, for example a polyvalent alkyl or aromatic group. The combination of the polyvalent organic moiety (A) and the linking groups (LG) forms the central moiety (CM) as previously described.

20 The central moiety can optionally contain other functional groups in addition to the pendant non-cyclic anhydride groups. For example, the central moiety may contain pendant acid groups, so that the anhydride is represented by the formula:

25



30 wherein m is the number of pendant acid groups and all others have the meaning previously given. The molar ratio of pendant non-cyclic anhydride groups to pendant acid groups in the oligomeric anhydride is preferably at

least about 25:75, more preferably at least about 50:50, and more highly preferably at least about 75:25. Most preferably, the anhydride contains substantially no pendant acid groups. The central moiety can also contain minor quantities of cyclic anhydride moieties.

5 The molecular weight of the anhydride resin is an important feature of the present invention, and should be less than about 3000. At molecular weights of the oligomeric anhydride greater than 3000, it is difficult to attain a sprayable composition with a volatile organic content of less than about 4.0 pounds of organic solvent per gallon of curable
10 compositions. The molecular weight of the anhydride resin is preferably about from 400 to 1,000, and the anhydride resin preferably has 3 to 4 pendant, non-cyclic anhydride moieties bonded to each central moiety.

 The oligomeric epoxy component contains at least two epoxy groups and should have a molecular weight of less than about 1500.

15 Typical epoxy components which may contain a hydroxy functionality or (OH) group include, among others, sorbitol polyglycidyl ether, mannitol polyglycidyl ether, pentaerythritol polyglycidyl ether, glycerol polyglycidyl ether, low molecular weight epoxy resins such as epoxy resins of epichlorohydrin and bisphenol-A, and polyglycidyl ethers of
20 isocyanurates, for example, "Denecol" EX301 from Nagase and DCE-358® sorbitol polyglycidyl ether from Dixie Chemical.

 Optional additional epoxy components which typically do not contain significant hydroxy functionality include, among others, di- and polyglycidyl esters of polycarboxylic acids, and di- and polyglycidyl esters of
25 acids, such as Araldite CY-184® from Ciba-Geigy, or XU-71950 from Dow Chemical are preferred since they form high quality finishes. Cycloaliphatic epoxies can also be used, such as ERL-4221 from Union Carbide.

30 Alternatively or additionally, the present compositions may contain, a polymeric epoxy resin having a molecular weight of from about 1,000 to 20,000. The epoxy resin can comprise, in addition to epoxy-group-containing monomers, copolymerized monomers of alkyl methacrylates or alkyl acrylates or mixtures thereof, where the alkyl groups have 1-12 carbon atoms. Optionally, the acrylic polymer can contain other components such

as styrene, alpha-methyl styrene, acrylonitrile, and/or methacrylonitrile in amounts of about 0.1 to 50 percent by weight.

Typical alkyl acrylates and methacrylates that can be used to form the anhydride acrylic polymer are as follows: methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, pentyl methacrylate, hexyl methacrylate, octyl methacrylate, decyl methacrylate, lauryl methacrylate, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, octyl acrylate, nonyl acrylate, decyl acrylate, lauryl acrylate and the like. Other components that can be used to form the acrylate polymer are acrylamide, methacrylamide, and acrylo alkoxy silanes such as gamma methacryloyl propyl trimethoxy silane. The polymer can optionally contain hydroxy functional copolymerized monomers such as hydroxyethyl acrylate, hydroxypropyl acrylate, and hydroxyethyl methacrylate.

Suitably the epoxy component can be present in the composition in the amount of 20 to 90 percent, by weight of binder, preferably 40 to 65 percent. However, a better determinative measure of the amount of each of the main or reactive components of the binder (which "binder" generally includes components other than solvent or carrier and pigments) is the equivalents ratio. In the compositions according to the present invention, the ratio of equivalents of hydroxy to anhydride is at least 0.05, preferably at least 0.1. In the absence of isocyanate, the range is 0.05 to 1.0. The range of the ratio of equivalents of hydroxy to the combination of anhydride and isocyanate, however, may suitably be about 0.05 to 1.5, preferably about 0.1 to 1.0, and most preferably about 0.3 to 0.8. The equivalents ratio of epoxy to anhydride is about 0.5 to 1.8, preferably about 0.7 to 1.4.

As mentioned earlier, the composition may optionally also contain an organic polyisocyanate crosslinking agent, for example in the amount of 0 to 25 percent by weight of binder, preferably 5 to 15 percent. Any of the conventional aromatic, aliphatic, or cycloaliphatic isocyanates; trifunctional isocyanates and isocyanate functional adducts of a polyol and a diisocyanate can be used. Typically useful diisocyanates are 1,6-hexamethylene diisocyanate, isophorone diisocyanate, 4,4'-biphenylene diisocyanate, toluene diisocyanate, bis-cyclohexyl diisocyanate, tetramethylene xylene diisocyanate, ethyl ethylene diisocyanate, 2,3-dimethyl ethylene diisocyanate, 1-methyltrimethylene diisocyanate, 1,3-

phenylene diisocyanate, 1,5-naphthalene diisocyanate, bis-(4-isocyanatocyclohexyl)-methane, 4,4'-diisocyanatodiphenyl ether and the like.

Typical trifunctional isocyanates that can be used are
5 triphenylmethane triisocyanate, 1,3,5-benzene triisocyanate, 2,4,6-toluene triisocyanate and the like. Trimers of diisocyanates also can be used such as the trimer of hexamethylene diisocyanate which is sold under the tradename "Desmodur"® N-3390 and the trimer of isophorone diisocyanate. Trifunctional adducts of triols and diisocyanates may be used.

10 The present compositions contain a functional amount of at least one active catalyst. By functional amount is meant a quantity which will allow for curing at ambient conditions. Particularly beneficial in the present invention are tertiary amine catalysts such as triethylene diamine (1,4-diazabicyclo(2.2.2)octane), bis(2-dimethyl aminoethyl)ether and
15 tetramethylethylenediamine. When the composition also comprises an isocyanate crosslinking agent, an additional catalyst, for example, a dibutyl tin dilaurate or dibutyl tin diacetate may be included.

The total amount of catalyst is suitably used in the amount of 0.05 to 5 percent by weight of binder.

20 The coating compositions of the present invention are usually formulated into high solids coating systems dissolved in at least one solvent. The solvent is usually essentially all organic and comprises 10 to 70 percent, preferably 20 to 60 percent by weight of the composition. Preferred solvents include aromatic hydrocarbons such as petroleum naphtha or
25 xylenes; ketones such as methyl amyl ketone, methyl isobutyl ketone, methyl ethyl ketone or acetone; esters such as butyl acetate or hexyl acetate; and glycol ether esters such as propylene glycol monomethyl ether acetate.

The coating compositions of the present invention can also
30 contain conventional additives such as pigments, stabilizers, rheology control agents, surface tension reducing agents, flow agents, toughening agents and fillers. Such additional additives will, of course, depend on the intended use of the coating composition. Fillers, pigments, and other additives that would adversely effect the clarity of the cured coating will not
35 be included if the composition is intended as a clear coating.

The compositions of the present invention usually have a volatile organic content of less than about 4.4 pounds of organic solvent per gallon of curable composition. The coating compositions are typically applied to a substrate by conventional techniques such as spraying, electrostatic spraying, roller coating, dipping or brushing. The present formulations are particularly useful as a clear coating for outdoor articles, such as automobile and other vehicle body parts. The substrate is generally prepared with a primer and or a color coat or other surface preparation prior to coating with the present compositions. The present coating compositions can be applied using conventional techniques such as wet-on-wet applications over solvent borne basecoats, or over dried waterborne basecoats. The ability to apply the present compositions by spraying techniques with the unusually low VOC content is surprising.

After application to a substrate, the present compositions are cured at ambient conditions (about 60 to 110°F, depending on the geographical location, usually 65 to 90°F).

The performance characteristics of the final cured coating composition are excellent, providing a combination of excellent gloss and durability to abrasion, sunlight and acidic rain. At the same time, the compositions provide low volatile organic content and ease of handling.

The present invention is further illustrated by the following specific examples, in which parts and percentages are by weight unless otherwise indicated.

25

EXAMPLE 1

This example illustrates the synthesis of a tetra-functional half-acid ester. The following constituents were charged to a reaction vessel equipped with a heating mantle, reflux condenser, thermometer, nitrogen inlet, and stirrer:

30

<u>Portion 1</u>	<u>Parts by Weight</u>
Pentaerythritol	478.0
Methyl hexahydrophthalic anhydride	2250.0
Triethylamine	0.5

Portion 2

Xylol (135-145°C)

2250.0

Total

4978.5

Portion 1 was charged into the reaction vessel, heated to 180°C under a nitrogen blanket and held for 30 minutes. After the hold period, the reaction mixture was cooled and Portion 2 added.

5

EXAMPLE 2

This example illustrates the preparation of a linear pendant anhydride (hereafter referred to as LPA). The solution prepared in example 1 was charged into a 5 liter flask equipped with a stirrer and a gas inlet tube. The gas inlet tube was attached to a ketene generator similar to the one described by Williams et al in the Journal of Organic Chemistry 5, 112, 1940. Ketene is bubbled through the solution until all of the acid groups have been converted to anhydride groups. Reaction progress is monitored via FTIR. Solvent was then removed under vacuum to give a linear pendant anhydride with the following characteristics:

15

Percent weight solids: 78.0

Anhydride eq. wt.: 329 ± 4 (on solution basis)Acid eq. wt.: 6176 ± 1323 (on solution basis)

20

EXAMPLE 3

This example illustrates the preparation of a polymeric epoxy resin containing hydroxy functionality. A skewed structure epoxy polymer was synthesized consisting of trimethyl silane protected hydroxy ethyl methacrylate / isobutyl methacrylate / glycidyl methacrylate in the mole ratio of 1 / 5 / 5. The following ingredients were dried over molecular sieves. The materials were charged to a clean, dry reactor.

25

ComponentParts by Weight

Tetrahydrofuran (anhydrous)

714.428

1-(2-trimethylsiloxy) ethoxy-1- trimethylsiloxy-2-methyl propene

80.143

Glycidyl methacrylate monomer	154.143
Iso-butyl methacrylate	51.285

5 The above solution was cooled to -5 degrees C. Cooling of the reaction mixture was stopped for the start of the exothermic reaction. The following solution was added over 30 minutes, stopping when the reaction begins to exotherm. Cooling was resumed when the exotherm raised the temperature to 10-15 degrees C. The next step was started when the charged monomer was 75% converted.

<u>Component</u>	<u>Parts by Weight</u>
Tetrabutyl ammonium chlorobenzoate	0.286
Tetrahydrofuran	0.571

10 The addition of both of the following solutions was started simultaneously. Solution 1 was added over 40 minutes and solution 2 was added over 30 minutes.

<u>Component</u> (Solution 1)	<u>Parts by Weight</u>
Tetrahydrofuran	2.143
Tetrabutyl ammonium chlorobenzoate	0.286

<u>Component</u> (Solution 2)	<u>Parts by Weight</u>
Glycidyl methacrylate	51.286
Iso-butyl methacrylate	154.143

15

Once complete conversion of the monomers occurred, the following ingredients were added in the order listed, distilling off 428.571 parts of excess solvent to give a yield of 800.0 parts of a polymer solution at 61% solids.

20

<u>Component</u>	<u>Parts by Weight</u>
Methanol	13.714
Glacial acetic acid	6.143

The intermediate was concentrated as follows:

<u>Component</u>	<u>Parts by Weight</u>
above intermediate	800
butyl acetate	189.8
glacial acetic acid	4.25

5 Finally, 313 parts of this reaction product was distilled out for a resulting solution of 65% solids.

EXAMPLE 4

10 This example illustrates an ambient cured LPA/ sorbitol ether epoxy composition system according to the present invention. Two separate parts or packages were formed and the parts mixed in a pot to obtain an ambient curing coating for application to a substrate.

Part I

<u>Component</u>	<u>Parts by Weight</u>
LPA (Example 2 above)	49.0
15% triethylene diamine / PM acetate	8.84
5% BYK-301® (silicone) / PM acetate	0.66
Butyl acetate	12.2

Part II

<u>Component</u>	<u>Parts by Weight</u>
DCE-358® sorbitol ether epoxy from Dixie Chem.	29.3

15 PM acetate is propylene glycol monomethyl ether. Parts I and II were combined in the amounts shown (total 100 parts), applied as a film to a substrate, and cured at ambient conditions. The coating showed good
20 appearance, cure, and film properties.

EXAMPLE 5

This example illustrates the preparation of a coating composition comprising an LPA/sorbitol ether epoxy and diglycidyl ester

blend. Two separate parts or packages were formed and the parts mixed in a pot to obtain an ambient curing coating for application to a substrate.

Part I

<u>Component</u>	<u>Parts by Weight</u>
LPA	56.64
5% BYK®-301 / PM acetate	0.7
25% Niax® A-99® (tertiary amine from Union Carbide) in PM acetate	8.69
PM acetate	2.7

5

Part II

<u>Component</u>	<u>Parts by Weight</u>
DCE-358® sorbital ether epoxy from Dixie Chem.	17.12
XU-71950® diglycidyl ester from Dow	14.15

- Parts I and II were combined in the amounts shown (total 100 parts), applied as a film to a substrate, and cured at ambient conditions.
- 10 The coating showed good appearance, cure, and film properties.

EXAMPLE 6

- This example illustrates an coating composition comprising LPA/ diglycidyl ester polymeric epoxy blend. Two separate parts or
- 15 packages were formed as follows, for subsequent mixture in a pot to obtain an ambient curing coating composition.

Part I

<u>Component</u>	<u>Parts by Weight</u>
LPA (Example 2 above)	45.3
5% BYK®-301 in PM acetate	0.56
15% triethylene diamine in PM acetate	9.06

20

Part II

<u>Component</u>	<u>Parts by Weight</u>
XU-71950	11.31

GMA Epoxy (Example 3 above)

33.77

Parts I and II were combined in the amounts shown (total 100 parts), applied as a film to a substrate, and cured at ambient conditions. The coating showed good appearance, cure, and film properties.

5

EXAMPLE 7

This example illustrates the preparation of an ambient curing coating composition comprising an LPA/sorbitol ether epoxy/isocyanate blend. Three separate parts or packages were formed and the parts were mixed in a pot to obtain an ambient curing coating for application to a substrate.

10

Part I

<u>Component</u>	<u>Parts by Weight</u>
LPA (Example 2 above)	47.44
15% triethylene diamine in PM acetate	12.85
1% Dibutyl tin dilaurate in MEK (methyl ethyl ketone)	1.39
1% BYK®-301 in PM acetate	3.53

15

Part II

<u>Component</u>	<u>Parts by Weight</u>
DCE-358 sorbitol ether epoxy from Dixie Chem.	28.37

Part III

<u>Component</u>	<u>Parts by Weight</u>
Tolonate HDT-isocyanate from Rhone Poulenc	6.42

Parts I, II and III were combined in the amounts shown (total 100 parts), applied as a film to a substrate, and cured at ambient conditions. The coating showed good appearance, cure, and film properties.

20

EXAMPLES 8 - 10

These examples illustrate a refinish clearcoat according to the present invention comprising a blend of LPA with sorbitol glycidyl ether and diglycidyl cyclohexane dicarboxylate and epoxy resin and HMDI isocyanate trimer.

	<u>Parts by Weight</u>		
	<u>8</u>	<u>9</u>	<u>10</u>
<u>Part 1</u>			
Linear Pendant Anhydride (Example 2)	106.37	53.08	105.35
BYK® 306 flow additive	0.40	0.40	0.40
PM Acetate	5.31	3.55	5.67
Tinuvin® 1130 from Ciba	4.65	4.47	4.64
Tinuvin® 123 from Ciba	3.10	2.98	3.10
<u>Part 2</u>			
DCE-358® epoxy from Dixie	33.72	0.00	26.76
Tolonate HDT®	0.00	0.00	13.38
Polymeric epoxy as in Ex. 3 except a 1/8/8 ratio of HEMA/IBMA/GMA	0.00	70.58	0.00
XU-71950® epoxy from Dow	27.87	47.05	22.12
<u>Part 3</u>			
25% triethylene diamine in PM acetate	18.58	17.89	18.57
Total	200.00	200.00	200.00

The compositions prepared above were tested as films drawn down on glass or on glass previously coated with a blue Chromabase® (from DuPont) solventborne basecoat. The Properties were as follows:

Appearance	OK	OK	OK
<u>Dry time (in hours)</u>			
Bk Dry Time #1 (free from dust)	1.0	0.50	1.25
Bk Dry Time #2 (dry to touch)	23	7.375	22
Bk Dry Time #3 (hard dry)	22.5	22.5	22.5
Bk Dry Time #4 (through dry)	23+	23+	23+
Persoz 5 day/7 day (hardness)			
on glass	92/143	15/45	67/93
on chromabase	41/51	37/52	38/48
Tukon 7 Day (hardness)			
on glass	4.80	1.10	2.13
on chromabase	1.60	1.12	1.40
MEK Double Rubs (solvent resistance)			
on glass	200+	200+	200+
on Chromabase® basecoat	200+	30	200+

Various modifications, alterations, additions, or substitutions of the components of the composition of this invention will be apparent to those skilled in the art without departing from the scope and spirit of this invention. This invention is not limited to the illustrative embodiments set forth herein, but rather the invention is defined by the following claims.

WHAT IS CLAIMED IS:

1. A coating composition, for curing under ambient conditions, comprising, by weight of composition, 10 to 70 percent organic solvent and
5 30 to 90 percent of a binder comprising:
 - (a) an anhydride resin having a molecular weight of less than about 3000 that contains (1) a central moiety, and (2) on average, more than one pendant, non-cyclic anhydride moiety bonded to each central moiety;
 - 10 (b) an oligomer or polymer crosslinker having a molecular weight of about 150 to 20,000 and having epoxy functionality of at least 2, at least a portion of which crosslinker has at least one hydroxy functionality; and
 - (c) a functional amount of at least one active catalyst,
15 wherein the ratio of equivalents of hydroxy to anhydride is at least about 0.05 and the ratio of equivalents of epoxy to anhydride is 0.5 to 1.8.
2. The composition of claim 1 further comprising an isocyanate crosslinking agent wherein the ratio of equivalents of hydroxy to the
20 combination of anhydride and isocyanate is 0.05 to 1.5.
3. A curable coating composition of claim 1 applied to a substrate.
- 25 4. A coated substrate of claim 3 wherein the substrate is coated with a pigmented base coat.
5. A coated substrate of claim 4 wherein the applied curable composition is substantially free from pigment.
30
6. A coated substrate of Claim 4 wherein the base coat is a water based coating composition.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US 95/07123

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G59/42 C09D163/00 C08L73/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08G C09D C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,94 11415 (DOW CHEMICAL) 26 May 1994 see claim 1 see page 3, line 11 - line 13 see page 9, line 18 - line 20 see page 10, line 18 - line 22 see page 9, line 31 - line 35	1,3-6
X	EP,A,0 598 131 (KANSAI PAINT CO. LTD) 25 May 1994 see claims 1,4 see page 6, line 50 - line 55	1,3-6
A	EP,A,0 257 512 (PPG IND.) 2 March 1988 see claim 1	1-6
E	WO,A,95 18166 (E.I. DU PONT DE NEMOURS AND CO.) 6 July 1995 see example 1	1,3-6

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

11 October 1995

Date of mailing of the international search report

27. 11. 95

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

O'Sullivan, T

INTERNATIONAL SEARCH REPORT

Intern. Application No
PCT/US 95/07123

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9411415	26-05-94	AU-B- 5361194	08-06-94
		CN-A- 1087652	08-06-94
		EP-A- 0668883	30-08-95
		US-A- 5428082	27-06-95
EP-A-0598131	25-05-94	AU-B- 660511	29-06-95
		BR-A- 9205464	21-06-94
		US-A- 5418297	23-05-95
		AU-A- 2956192	28-06-93
		WO-A- 9311188	10-06-93
		NZ-A- 247076	22-12-94
EP-A-0257512	02-03-88	US-A- 4732790	22-03-88
		US-A- 4755582	05-07-88
		AU-B- 582308	16-03-89
		AU-B- 7732187	17-03-88
		CA-A- 1335341	25-04-95
		DE-D- 3787693	11-11-93
		DE-T- 3787693	28-04-94
		ES-T- 2059331	16-11-94
		JP-B- 6021275	23-03-94
		JP-A- 63084673	15-04-88
WO-A-9518166	06-07-95	NONE	

LOW VOC REFINISH COATING COMPOSITION

Patent Number: WO9601864
Publication date: 1996-01-25
Inventor(s): BARSOTTI ROBERT J (US); HARPER LEE R (US)
Applicant(s):: DU PONT (US); BARSOTTI ROBERT J (US); HARPER LEE R (US)
Requested Patent: ☐ WO9601864
Application Number: WO1995US07123 19950616
Priority Number(s): US19940272343 19940708
IPC Classification: C08G59/42 ; C09D163/00 ; C08L73/02
EC Classification: C08G59/42, C08L73/02, C09D163/00, C09D133/06B6
Equivalents: BR9508713, CA2192948, CN1176649, ☐ EP0770103 (WO9601864), JP10502686T

Abstract

A coating composition based on low molecular weight anhydride resin having pendant, non-cyclic anhydride moieties, hydroxy-functional epoxy resin, and active catalyst exhibits excellent performance characteristics as a coating cured at ambient conditions.

Data supplied from the esp@cenet database - I2

THIS PAGE BLANK (USPTO)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)